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CHAPTER XXXII

METALLURGY OF SODIUM

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CHAPTER 32

METALLURGY OF SODIUM115 Properties and Application of Metallic Sodium

Sodium and potassium were the first metals electrolytically produced using a voltaic pile by Humphrey and Davy in 1807 from fused NaOH and KOH.

Of all the alkali metals sodium has the greatest technical importance. Table 86 lists some of the properties of sodium, a soft metal that can easily be cut with a knife. The specific gravity of sodium is 0.97.

TABLE 86

PROPERTIES OF SODIUM

CHARACTERISTIC FEATURES	MAGNITUDE
Atomic weight	22.997
Valence	1
Specific gravity at 20° Centigrade	0.97
Temperature of Fusion	97.7°
Boiling Point	880°
Electrode potential relative to hydrogen	
□ electrode	-2.45
Electrochemical equivalent, grams per	
□ ampere-hour	0.858

Metallic sodium is extremely active chemically and decomposes water, forming hydrogen. With considerable sodium this reaction is explosive. As has been stated elsewhere, sodium is used as a reducing agent for separating aluminum and magnesium from their compounds.

Metallic sodium is readily oxidized upon exposure to air and becomes coated with an oxide Na_2O which in the presence of moisture is transformed into NaOH. This, in turn, reacting with atmospheric CO_2 , is converted into Na_2CO_3 . To guard against oxidation, sodium is preserved

in kerosene or gasoline. Sodium finds wide industrial applications in the production of sodium peroxide, cyanide, synthesis and dehydration of organic substances. Certain bearing alloys contain up to 2-3 percent of sodium. Metallic sodium is of great importance in the so-called process of silumin modification. Small additions of sodium give silumin a fine crystalline structure, producing beneficial changes in the alloy's properties. As a light metal, sodium has been widely used in the United States. The Dow Chemical Company employed an iron conduit filled with sodium to transmit high electrical current at low potentials. Such a conduit weighs only one-third as much as a copper conduit of equal current-carrying capacity.

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6g 2. Humphrey Day

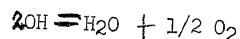
The industrial production of metallic sodium is effected through the electrolysis of molten caustic soda or sodium chloride. The electrolysis of molten caustic soda was first performed by Castner in 1890. His original apparatus, although improved, is still used. Castner's electrolyzer for the electrolysis of caustic soda is shown in Figure 214 (Castner's Electrolyzer for the Production of Metallic Sodium). The electrolyzer consists of an iron boiler (crucible) inside of a brick shell. To preserve the molten caustic soda in the boiler, the latter is heated by gas burners G. From underneath, through the narrow portion of the boiler, passes a bronze cathode B, which is covered by an iron cylinder D. The bottom of the cylinder is a wire-nickel screen, which surrounds the cathode and separates it from the cylindrical nickel anode.

The electrolytically produced metallic sodium floats to the top and accumulates inside the cylinder D, where it is extracted by means of a perforated ladle, with caustic soda being added periodically. The chemical reactions which take place during the electrolysis of molten caustic soda are quite simple. The sodium anion is discharged at the cathode, with the resultant separation of metallic sodium. At the anode, the

hydroxylions are discharged with a corresponding formation of water and free oxygen, which is deposited at the anode.

At the cathode: $2\text{Na}' + 2\text{e} = 2\text{Na}$

At the anode: $2\text{OH}' - 2\text{e} = 2\text{OH}$



The water is formed at the anode and is capable of passing through to the cathode, and the cathode sodium of passing toward the anode. This process is sometimes accompanied by the complications of a reaction between sodium and water to form NaOH with a consequent reduction of the sodium output--attended by the liberation of hydrogen. Hydrogen and oxygen : $2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2$ forms an explosive mixture.

Water present in the caustic soda is also electrolyzed to liberate oxygen and hydrogen at the anode and cathode respectively. Hydrogen is usually conducted away from the cathode through a small opening in the cover of the electrolyzer and is burned in the air. Practical electrolyzers operate at 1200-1250 amperes and 4.5-5 volts. The temperature of the entire process is kept between 310-320 degrees at which temperature the specific gravity of fused NaOH is 1.79, its specific electric conductivity being 2.12 reciprocal ohms and the dissociation voltage being equal to 2.22 volts. The entire process takes place with the anode and cathode current densities of 1.5 and 2.0 amperes per square centimeter, respectively. After a while the electrolyte becomes saturated with Na_2CO_3 , etc., and therefore must be periodically replaced. Sodium yield for given current by Castner's method averages about 40 percent with a d.c. electrical power expenditure of 14,000-15,000 kilowatt-hours per ton of sodium.

The first experiments dealing with the electrolysis of molten sodium chloride to obtain metallic sodium were conducted by Faraday in 1833. Subsequently, in view of the inexpensiveness and good supply of basic materials, this process attracted attention for further industrial development. However, a whole train of difficulties had to be overcome, the most important of which are the closeness of the NaCl melting point

of (800 degrees) and the boiling point of metallic sodium (880 degrees), as well as the low specific gravity and readiness of the metal to be oxidized.

For purposes of technical electrolysis, a number of electrolyzers suggested solved this problem in a more or less satisfactory fashion. Here, we shall discuss one of the latest and most improved electrolyzers of fused NaCl due to Downes (Figure 215, Downes' Electrolyzer for the Separation of Sodium Through the Electrolysis of NaCl.) The electrolyzer consists of an iron casing 1 of rectangular or square cross-section lined with fire-resistant material 2. The centrally located graphite anode A is surrounded by a ring-shaped cathode K and with a mesh diaphragm B, which separates the anode from the cathode. Above the anode is shown a funnel 4 terminating in a gas pipe 5 to conduct the liberated Cl_2 away from the anode. Cathode-deposited metallic sodium is collected in the ring-shaped space 6 and, after passing through pipe 7, is collected in the container 8. The surface of the electrolyte is covered with a thin crust of frozen electrolyte, on top of which are placed fresh ^{Quantities} ~~batches~~ of NaCl delivered through the opening 9. The electrolyzer voltage in the case of NaCl is higher than the ^Y voltage for NaOH electrolysis; however, in this case, the output for a given current is also higher than for NaOH and averages 75 percent. Therefore, the expenditure of electric energy in this case does not exceed that of Castner's process and is between 14,000-16,000 kilowatt-hours per ton of sodium. The advantages of this method as compared with Castner's are the cheapness of the electrolyte and the collection of chlorine gas as a by-product.